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# Room-temperature hydrogen gas sensor

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The hydrogen gas sensing ability of *n*-type PtSi/porous Si Schottky junctions is investigated at room temperature. These junctions exhibit a breakdown-type current-voltage curve, whose breakdown voltage depends on the gas content inside the pores. Hydrogen replaces gases with an inherent dipole moment and increases the breakdown voltage. The response time is very fast, around 6 s, and the recovery time is about 60 s. Concentrations as low as 10 ppm have been detected in the presence of methanol and acetone. Detection has been tested at different temperatures ranging from 273 to 300 K. © *2005 American Institute of Physics*. [DOI: 10.1063/1.2077865]

Hydrogen sensing has been the subject of much research in recent years.[1–3] Industrial applications—which deal with the use, transportation, and storage of hydrogen as well as the automotive industry, investing heavily in hydrogen fuel cells as a pollution-free alternative to today's internal combustion engines—need rugged, stable, durable, and compact sensors for standard leak detection and also area monitoring. Several different types of detectors, working based on varied physical and chemical properties, have been suggested[4–10] ranging from metal-oxide gas sensors to ChemFET, and transient response devices.[11] Of prime importance is the fact that hydrogen is to be detected in air and in the presence of other combustible hydrocarbons and alcohols.[3] Selective hydrogen detection based on different types of molecular membranes or filters have been suggested.[12,13]

We have recently shown that *n*-type PtSi/porous Si Schottky junctions are able to sense certain gases, such as CO, $CO_2$, and $O_2$, at room temperature.[14] The reverse bias current-voltage (*I-V*) curve of these junctions exhibits a breakdown-type behavior at small reverse bias voltages of about 10 to 15 V, for the typical porosity levels of about 50% to 70%. Breakdown-type behavior has been attributed to the large fringing fields developed at the sharp edges of the porous surface which can be orders of magnitude larger than that of a smooth area Schottky junction under the same conditions.[15,16] It seems that gases with inherent dipole moment change the strength of the electric fringing fields and decrease the breakdown voltage. Gases without a dipole moment affect the *I-V* curve by replacing the gases inside the pores which have dipole moment. These types of gases increase the breakdown voltage.[14]

In this letter, we propose these junctions as novel hydrogen sensors, which can detect hydrogen at room temperature and below. When hydrogen is introduced, the ambient gas inside the pores is replaced and the breakdown voltage increases. The low-temperature operation of these detectors as well as their fast response and recovery time could be of great practical interest. These detectors offer a certain degree of selectivity as they are not sensitive to ethanol, methanol, or acetone.

*n*-type Si wafers which were (100) oriented, with a resistivity in 13–33 Ω cm range were used. Anodic etching was performed under ultraviolet radiation in a solution containing HF, deionized water, and ethanol (25, 25, and 50%) to produce the porous samples. Application of a current density of 50 mA/cm$^2$ for 20 min results in 70% porous samples. Scanning electron microscope (SEM) micrograph of such a sample is provided in Fig. 1. The pores size is about 2–5 $\mu$m and their depth is about 3 $\mu$m. The porous surface to which gas is exposed was 0.5 cm$^2$ and the pore size, depth, and distribution were uniform (and reproducible) across the samples. Pt was electrodeposited into the pores using a solution containing $H_2(PtCl_6).6H_2O$ 4g/liter, $(NH_4)2HPO_4$ 20 g/liter, $Na_2HPO_4$ 100 g/liter, at 90 °C. Electrodeposition was performed by applying 20 mA of current for 45 min which deposited a thick Pt layer into the pores filling them completely. The samples were subsequently annealed at 400 °C for 20 min to create a thin PtSi layer. Under such annealing conditions, the thickness of the PtSi layer had been estimated to be between 20 to 100 Å.[15] The excess unreacted Pt which fills the pores was then removed using a standard solution.[15] This leaves empty pores behind. The ambient gas, therefore, fills the pores and reaches the PtSi layer which has uniformly covered the pore

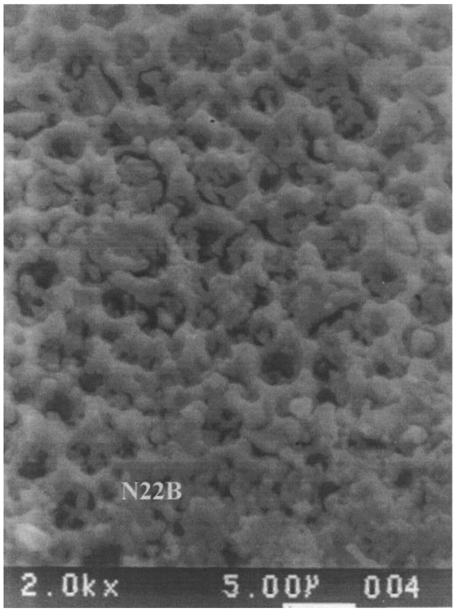

FIG. 1. SEM micrograph of a porous sample. The pore sizes vary between 2 to 5 $\mu$m and the their depth is about 3 $\mu$m (which is not shown in the figure).

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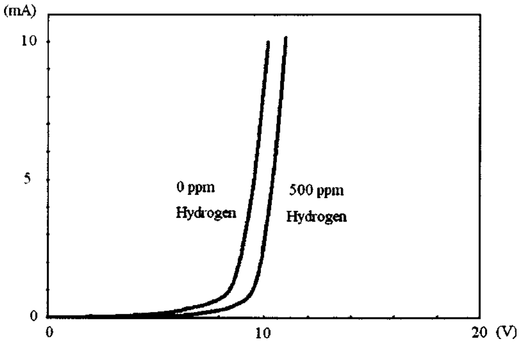

FIG. 2. *I-V* curve of a sample in 15% humid air with no hydrogen and in the presence of 500 ppm of hydrogen at room temperature. *I-V* curve moves to larger voltages as hydrogen is introduced. It reaches its maximum at 500 ppm of hydrogen, after that it remains unchanged.

walls. Connections were made to the PtSi layer and to the substrate. For the tests which are carried out in air, we use two closed gas chambers. The samples are placed inside one cylindrical chamber which has an exact volume of 30 $\times 10^3$ cm$^3$. Normal air is let inside the chamber to atmospheric pressure. The air humidity is checked by a standard humidity sensor, which for these experiments was 15% (we have not introduced water vapor to change the humidity in these measurements). This chamber is then isolated. A second smaller chamber with a volume of 150 cm$^3$ is first connected to a turbomolecular pump and its pressure is brought down to $10^{-5}$ Pa. Then selected gases are let inside the chamber to a predetermined pressure. This chamber is then disconnected from the turbopump and is connected to the larger chamber in which the sample is placed. The relative concentration is then calculated considering the volume of the two chambers and their pressure before connection.

The reverse bias *I-V* curve of this device at 300 K in air and in presence of 500 ppm hydrogen gas is provided in Fig. 2. As observed, *I-V* curve moves to larger voltages as hydrogen is introduced. In other words, the breakdown voltage increases with hydrogen gas content. The change in the breakdown voltage with hydrogen concentration is provided in Fig. 3. We estimate an error of about 4 ppm in our measurements. At 10 ppm of hydrogen concentration, the breakdown voltage increases by about 0.02 V. The change in breakdown voltage follows more or less a piecewise linear curve. It saturates at about 500 ppm after which no change in breakdown voltage is exhibited.

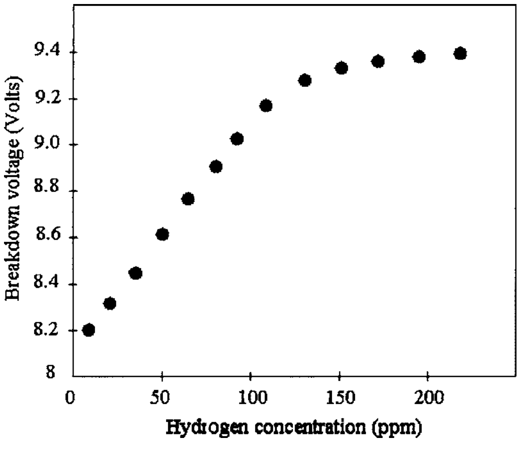

FIG. 3. The change in breakdown voltage as hydrogen concentration is increased from zero. The relation can be estimated as a piecewise linear curve which saturates at 500 ppm (not shown here).

When doing measurements, the samples are placed upside down attached to the top cover of the gas enclosure. It is possible to obtain larger sensitivity to gas with a funnel-type top cover, in which the sample is placed at the tip. For example, for the funnel shape top cover, the change in breakdown voltage due to 10 ppm of hydrogen is equal to 100 ppm of hydrogen in the regular gas enclosure. This is because the effective hydrogen concentration is increased at the sample surface as hydrogen replaces more air molecules in this case.

The response and recovery times were estimated to be around 6 and 60 s, respectively, which are quite fast and are due to the physical nature of the detection mechanism. The longer recovery time may be due to hydrogen adsorption, which take longer to be released. The same is observed for other gases.[14]

The experiments were also carried at lower temperatures down to 273 K and hydrogen gas sensitivity was exhibited in a similar fashion. The change in the *I-V* curve was similar to Fig. 2. Temperatures lower than 273 K were not tried because water vapor condenses on the sample and shields it from hydrogen.

As was mentioned, it is very important to check hydrogen sensing in the presence of other reducing gases; therefore, experiments were carried out in the presence of different concentrations of acetone, methanol, and ethanol up to 2000 ppm. The introduction of these gases did not have any affect on the hydrogen gas sensing behavior. In other words, these samples are able to sense hydrogen even in the presence of a large concentration of acetone, methanol, or ethanol. It seems that acetone, methanol, and ethanol cannot replace the gas content inside the pores perhaps because of their large size and mass. As a result, they do not affect the *I-V* curve and do not interfere with hydrogen gas sensing.

Durability of these samples was tested by biasing them below their breakdown voltage and exposing them to hydrogen gas periodically. The samples have not shown any drift in *I-V* curve for a period of 3 months. A current limit of 5 mA was set on the biasing circuit. Larger currents resulted in a drift in *I-V* curve and caused some samples to be burnt.

We have demonstrated here that *n*-type PtSi/porous Si Schottky junctions are capable of detecting hydrogen gas at room temperature. Detection occurs in air and in presence of hydrocarbons, such as acetone, methanol, and ethanol. The detection mechanism is physical in nature, in which hydrogen replaces ambient gas inside the pores and this changes the electric fringing fields. This results in a relatively fast response and recovery times. The physical nature of detection mechanism also makes low-temperature operation possible. The detector is stable, robust, compact, easy to fabricate, and is compatible with integrated circuit fabrication technology.

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